

SYMPOSIUM ON STABILITY AND OXIDATION OF MIDDLE-DISTILLATE FUELS  
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ANALYSIS OF SOLIDS FORMED DURING THERMAL- AND  
STORAGE-STABILITY TESTING OF JET FUELS  
DERIVED FROM PETROLEUM AND FROM COAL

By

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INTRODUCTION

Recently, the Department of Energy and the Air Force began a program to investigate the production of jet fuel and other commercial products from the gasification of lignite at the Great Plains Gasification Plant (GPGP), Beulah, North Dakota. This project was undertaken to increase the economic viability of the plant and, at the same time, to create a reliable source of jet fuel for Air Force bases in the northern great plains area (1). In cooperation with DOE and the Air Force, the National Institute for Petroleum and Energy Research (NIPER), has investigated the thermal and storage stability properties of a JP-8 jet fuel produced from GPGP liquid by-products and compared these properties with those of a conventional JP-8 fuel derived from petroleum.

Several decades of investigations on fuel stability have increased our knowledge of the chemistry involved in fuel degradation. Most of these studies have been focused on trace heteroatomic components in fuels (2-16). In the past, ambient storage stability and high temperature thermal stability have been viewed as two separate issues, especially when trace contaminants have been considered. However, our recent findings on petroleum-derived jet fuels indicate that hydrocarbons in neutral fractions from relatively clean fuels are susceptible to oxidative degradation at high temperatures and under ambient storage conditions (10).

Hydrocarbon types that seem to be emerging as important in fuel degradation are the cycloalkylaromatics, such as indans and tetralins (11). These types are abundant in many coal liquids, including the hydrotreated tar-oil distillates from GPGP. In this respect, determination of the thermal and storage stabilities of jet fuel produced from lignite or coal is significant.

Perhaps the most undesirable consequence of fuel degradation is the formation of solids. Thus, a logical approach in studying degradation is to investigate the compositions of the solids formed under ambient storage conditions and at high temperatures to which the fuel might be subjected in a turbine engine. We have used separation procedures and identification methods, particularly HPLC and mass spectrometry, to analyze solids formed under simulated-storage and high-temperature conditions (11,17-21). Two fuels were studied in the present investigation: a coal-derived fuel and a conventional fuel from petroleum. A comparison of results from these two fuels is reported.

#### EXPERIMENTAL

The two fuels studied were a JP-8 (NIPER No. 2987) produced from GPGP liquid by-products (No. 89-WEH-157) and a petroleum-derived reference JP-8 (NIPER No. 2955).

The storage stability of both fuels was determined by two different methods. In the first, samples were aged at 80° C under 100 psig oxygen for 1, 2, 3, and 4 weeks. In the second, aging was performed by ASTM method D 2274, in which oxygen was bubbled through the samples for 16 and 40 hours at 95° C.

The sediment produced by aging the coal-derived fuel at 80° C was characterized by separation into six fractions using an HPLC acid-fractionation method developed at NIPER in other investigations (17,18). Compound types were separated into fractions of increasing acidity.

Both fuels were subjected to thermal-stability testing in a jet fuel thermal oxidation tester (ALCOR, Inc., San Antonio, TX) using ASTM method D 3241 (JFTOT test). Breakpoints were also determined for each fuel. The fuels were then stressed for extended periods of time at 10° C above the breakpoint to generate sufficient solids on the heated tube and on a downstream filter to permit mass-spectral analysis (20,21).

For extended runs, the fuel-flow system of the JFTOT apparatus was modified so that the fuel passed from the heated test section through a 25 mm diameter membrane filter to a variable-speed pump and then to a spent-fuel reservoir. A fuel-flow rate of 1 mL/min was used (20,21).

In the first extended test with the 2955 reference fuel, a nylon filter with a pore size of 0.45  $\mu$ m was used to collect the filterable solids. The tube temperature was 280° C. After seven hours, the filter plugged and the experiment was stopped. For the second extended run with the same fuel, a glass-fiber filter, type GF/F, with a 0.7  $\mu$ m pore size was used. A ten-hour run gave no detectable plugging. However, when the apparatus was disassembled, the filter was found to be partially disintegrated. In the extended JFTOT run with the coal-derived fuel (2987), the tube temperature was 310° C. A nylon filter with a pore size of 0.45  $\mu$ m was used, and after 17 hours it became plugged. The JFTOT tubes and filters from the experiments with both fuels were saved for analysis by mass spectrometry.

The mass-spectrometric method used in the analyses of the JFTOT tube deposits and filterable sediments was developed previously as part of a similar investigation on fuel stability (19,20). Probe microdistillation/mass spectrometry (PMD/MS) was used to provide high resolution mass spectra of the solids, and the data were analyzed to produce curves of ion intensity vs. temperature or time (elimination curves) for ions identified with specific elemental formulas (19).

Deposits on the JFTOT tubes were sampled by machining their surfaces in a lathe using a cleaned tool bit (20). Turnings containing each deposit were then placed in a temperature-programmed quartz probe for introduction under PMD/MS conditions into a Kratos MS-50 high resolution mass spectrometer (Kratos Analytical Instruments, Manchester, U.K.). Probe temperature was increased linearly at 10° C/min. Twenty to thirty spectra were recorded at a resolving power of 10,000 to 20,000 over a temperature range from ambient to greater than 400° C. Seventy eV electron impact was used for ionization to maximize the signal-to-noise ratio on mass-spectral peaks being formed from a limited amount of sample. Mass spectra were not recorded below  $m/z$  70.

Sediments on the filters used with the JFTOT apparatus were sampled by cutting small filter strips for introduction by probe into the mass spectrometer (20). Using this approach, spectra of the filterable sediments were recorded under the same conditions as given for the tube deposits, except that 25 eV electron impact was used for ionization of the sediment from fuel 2955. The lower-energy ionization was selected to suppress intensities of fragment-ion peaks, but this method did not appear to offer any advantage over 70 eV electron impact and was not used with the other samples. To avoid thermal decomposition of the nylon filter used with fuel 2987, the probe temperature was limited to approximately 300° C.

## RESULTS AND DISCUSSION

**Initial Fuel Characterization.** Results from the initial characterization of both fuels are shown in Table I. The coal-derived fuel (No. 2987) showed a very slight color that may have been caused by suspended clay. This also explains the relatively long filtration time for the fuel. Both fuels easily met the viscosity specification, and both passed the simulated distillation test (results not shown), except for slightly exceeding the maximum value for the endpoint temperature. The simulated distillation also showed that the coal-derived fuel contained more low-boiling components than the reference fuel. No peroxides were detected in the reference, but the coal-derived fuel showed a trace (0.5 ppm).

**Storage Stability.** Table II summarizes results from the storage stability experiments. The coal-derived fuel (2987) showed lower sediment formation through three weeks of storage at 80° C under 100 psig oxygen. However, the peroxide content in 2987 was consistently higher than in the reference fuel (2955) and reached a maximum at approximately three weeks. Between three and four weeks, the coal-derived fuel deteriorated significantly. A large quantity of sediment was formed and the fuel darkened. After three weeks, the peroxide content in 2987 decreased somewhat, as has been observed in storage-stability testing with other fuels.

The oxidation-stability test (ASTM D 2274) on the two fuels gave similar results (not shown) to those obtained from the storage stability test. Through 40 hours, the coal-derived fuel showed less sediment formation and color than the reference fuel. Peroxide values were somewhat higher in the coal-derived fuel.

**Fractionation by HPLC of Sediment Formed During Storage-Stability Testing of Coal-derived Fuel.** The sediment produced by aging the coal-derived fuel for four weeks at 80° C under 100 psig oxygen was characterized by separation into six fractions using an HPLC acid-fractionation method (17,18). Yields of the fractions, which are separated according to increasing acidity, are given in Table III along with compound types typically present in each fraction. Any neutral or basic compounds would be expected in fraction 1 together with very weak acids. The relatively low recovery of 78.74% is attributed to loss of material in the work-up of fraction 6 and possible retention of very polar substances on the HPLC column. The yield data show that the bulk of the sediment was separated into fractions 5 and 6, which typically contain carboxylic acids and difunctional acids, respectively.

**Thermal Stability.** Results from the JFTOT test (ASTM D 3241) of the reference fuel (2955) and coal-derived fuel (2987) are given in Table IV. Both fuels easily met the specifications. Fuel 2987 was stable to a higher temperature than fuel 2955, as determined by the breakpoint temperatures of 295° C and 275° C, respectively.

**Mass-Spectral Analysis of JFTOT Tube Deposits and Filterable Sediments.** To make a reasonable comparison of results obtained from a large amount of mass-spectral data, abbreviation in tabulated form is used to discuss compound types identified in the solids formed during fuel degradation. Each table lists ions detected in homologous series corresponding to a particular elemental formula. For example, ions arising from hydrocarbons are classified as having  $C_nH_{n+Z}$  formulas where Z ranges from +2 to -23. Thus, molecular ions for alkylbenzenes ( $C_nH_{2n-6}$ ) are listed under a Z number of -6. Major fragment ions are given along with molecular ions. These occur in series having a Z number one less than the number for molecular ions. For alkylbenzenes, fragment ions thus occur in the  $C_nH_{2n-7}$  series (Z number of -7). No ion intensities are given, but the prominence of homologues in a particular series can be estimated from the number of molecular and fragment ions detected for the series. The molecular mass of the first member of a series is identified with the parent compound, e.g., 78 with benzene in the alkylbenzene series. If the first ion detected in a molecular-ion series has a mass less than the mass listed for the parent compound, the ion may arise by rearrangement or it may belong to a series for another type not identified. In either case, the fact that the ion cannot be a molecular ion in the listed series is mentioned in a footnote to the table.

It is necessary to emphasize that names of compound types given in the first column of the tables are intended to be suggestions only. Undoubtedly, many of the ions having the specified elemental formulas do arise from the type indicated; however, others may originate from types not identified. In the discussion that follows, names are restricted to those given in the tables with the understanding that ions in the series can originate from other compound types, as well.

**Analysis of Filterable Sediment and Tube Deposit from Coal-Derived Fuel.** Numerous compound types were detected in the solids formed during thermal stressing of the jet fuel from coal, including those containing only carbon and hydrogen as well as heteroatomic types containing oxygen and nitrogen. Only traces of compounds containing sulfur were found.

In Table V identification of hydrocarbons in the filterable sediment and tube deposit is presented for the thermal degradation of fuel 2987. A broad range of aliphatic and alicyclic compound types was found in both solids. No molecular ions for alkanes were identified (nor were they expected), but fragment ions corresponding to alkyl groups were found over a mass range extending to  $m/z$  155 in the spectra from the sediment and to  $m/z$  183 in the spectra from the tube deposit. These fragments may have arisen from alkanes or from other compound types having alkyl side chains. Numerous molecular and fragment ions were recorded for olefins, dienes, cycloalkanes, cycloalkenes, and bicycloalkanes. These compound types were distributed rather uniformly between the tube deposit and the filterable sediment. For example, molecular ions for dienes, cycloalkenes, and bicycloalkanes were detected from  $m/z$  68 to  $m/z$  194 in the spectra from both solids. The ions appeared in the spectra over a broad range of probe temperatures, indicating that they arose from surface desorption and by covalent bond rupture, i.e., by pyrolysis.

Many molecular and fragment ions from aromatic hydrocarbons were detected in the spectra from the filterable sediment and tube deposit. Alkylbenzene homologues were identified in the sediment to 190 amu and in the tube deposit to 162 amu. Indans and tetralins were found in both solids with molecular masses extending to 188 amu. Aromatics with a greater degree of unsaturation were evident in both sets of spectra. Six members of the naphthalene series ( $Z$  number of -12) were identified in the sediment spectra and five members in the spectra from the tube deposit. The most highly aromatic types identified in either set of spectra were the fluoranthenes and pyrenes ( $Z$  number of -22). One member of the series, the parent compound at  $m/z$  202, was identified in the spectra of the sediment, and three members ( $m/z$  202, 216, and 244) were found in the tube-deposit spectra.

A number of molecular and fragment ions containing one oxygen were identified in the spectra from the filterable sediment and tube deposit. These are seen in Table VI. Molecular ions for aliphatic and alicyclic types (e.g., tetrahydrofurans) were almost nonexistent in the spectra, and they were not expected based on the known fragmentation of these compounds. However, a number of fragment ions for aliphatic and alicyclic oxygen-containing types were detected, as noted in the table.

Aromatics containing one oxygen were readily detected in both sets of spectra. Several phenols were identified, as well as a number of more unsaturated types, including naphthols and dibenzofurans. Compounds with a greater degree of unsaturation appeared to be partitioned more toward the filterable sediment than toward the tube deposit. As an illustration, four fluorenones and phenalenones (parent mass of 180) were detected in the sediment, but none were found in the tube deposit.

Compound types containing two oxygens were identified in the spectra of the filterable sediment and tube deposit, including nonaromatic and aromatic carboxylic acids and dihydroxyaromatics (results not shown). The aromatics were decidedly partitioned more toward the sediment. For example, six benzoic acids and benzodioxoles were found in the spectra of the sediment ranging from the parent compound ( $m/z$  122) to homologues having five alkyl carbons attached ( $m/z$  192). On the other hand, in the spectra of the tube deposit only one fragment ion attributable to these compound types was detected ( $m/z$  149). Although molecular ions containing two oxygens were detected in Z series as negative as -18 in the spectra of the sediment, no molecular ions in series more negative than -4 were detected in the tube-deposit spectra.

Table VII shows ions detected in homologous series for compounds containing three oxygens. Because of the more complex nature of these types, names are omitted except to note that the ions are attributable to multifunctional compounds. Phthalates are indicated by  $m/z$  149 in the -11 Z series. These compounds, especially dioctylphthalate, are common artifacts seen in mass spectra.

A very prominent peak appeared in the spectra of the tube deposit at  $m/z$  129, corresponding to a fragment ion of elemental formula  $C_6H_5O_3$ . It must have arisen from a nonaromatic oxygen-containing compound, such as an alcohol, ether, or peroxide. None of these compound types would produce a significant molecular ion. At first glance,  $m/z$  129 might appear to have an elemental formula of  $C_6H_7N$ , corresponding to quinoline or isoquinoline. However, the accurately measured mass of the peak was consistently closer to the value expected for the  $CHO_3$  combination (129.0552) than for the  $CHN$  combination (129.0578). Therefore, a formula of  $C_6H_7N$  was ruled out. The  $C_6H_5O_3$  ion at  $m/z$  129 was much weaker in the spectra of the filterable sediment, showing that the corresponding compound(s) was strongly partitioned toward the tube deposit.

Except for compound(s) producing the  $m/z$  129 peak, types containing three oxygens were partitioned more toward the sediment than toward the tube deposit. This is evident from the larger number of molecular and fragment ions found for the sediment as compared with the number found for the tube deposit. The difference is not easily explainable, but it may result from the relatively low thermal stability of compounds containing alcohol or ether groups; that is, these compounds may have appeared in smaller quantities in the tube deposit because they may have been thermally decomposed on the hot metallic surface of the tube.

A number of compounds containing one nitrogen were identified in the filterable sediment, but only a few were found in the tube deposit, as seen by comparing results in Table VIII. The difference may have been a consequence of thermal decomposition of nitrogenous compounds on the hot tube surface. Compound types prominent in the spectra of the filterable sediment included pyrrolines (molecular ions from  $m/z$  69 to 125 and 153) and aromatic types such as pyridines (or anilines), showing molecular ions from  $m/z$  79 to  $m/z$  149. Indolines, indoles, and quinolines (or isoquinolines) were abundant, as indicated by the number of molecular and fragment ions detected in homologous series for these types.

**Analysis of Filterable Sediment and Tube Deposit from Petroleum-derived Fuel.** In spite of the different origins of fuel 2987 (coal liquid) and fuel 2955 (petroleum), mass-spectral analyses of solids formed by thermally stressing the two fuels produced surprisingly similar results. Therefore, discussion of the compositions of the filterable sediment and tube deposit from fuel 2955 is limited mainly to differences found between the solids formed from the two fuels.

Numerous hydrocarbons were identified in the filterable sediment and tube deposit from fuel 2955. When these were compared with hydrocarbons from fuel 2987, it became evident that the compositions of the hydrocarbons in the solids from the two fuels were very similar. This observation suggests that the same hydrocarbons were contributing to the formation of the solids in both fuels.

Compound types having one oxygen were identified in the filterable sediment and tube deposit from fuel 2955. When compared with the same types identified in the solids from fuel 2987, only slight differences were seen that may not be significant. For example, only one dibenzofuran (mass 196) was detected in the sediment from fuel 2955, but in the sediment from fuel 2987 four homologues were found (masses 168 to 210), as noted in Table VI. Several fluorenones and phenalenones were detected in the tube deposit from fuel 2955 but not in the sediment from the same fuel. The opposite was found for fuel 2987, i.e., fluorenones and phenalenones were detected in the sediment but not in the tube deposit (Table VI).

Fewer compounds containing two oxygens were found in the filterable sediment from fuel 2955 than in the sediment from fuel 2987. Differences were particularly evident for the more unsaturated species. No types with Z numbers more negative than -12 (coumarins and dihydroxynaphthalenes) were detected in the 2955 sediment, whereas in the sediment from fuel 2987, types with Z numbers as negative as -18 were identified (biphenylene carboxylic acids and hydroxyfluorenones). In contrast, by comparing results from the two tube deposits, it was evident that more types containing two oxygens, especially aromatics, were detected in the tube deposit from fuel 2955 than in the 2987 deposit.

A very similar distribution of compound types containing three oxygens was found between the filterable sediments from the two fuels as well as between their tube deposits. As mentioned previously, a very strong  $m/z$  129 peak of elemental formula  $C_6H_9O_3$  was found in the spectra of the tube deposit from fuel 2987 (Table VII). This same peak was present in the spectra of the 2955 tube deposit although its intensity was not as strong as in the 2987 spectra. The  $C_6H_9O_3$  ion was also detected in the spectra of the filterable sediment from fuel 2955; however, its intensity was much weaker than in the spectra of the tube deposit from the same fuel.

Ions containing one nitrogen were identified in the spectra of the filterable sediment and tube deposit from fuel 2955. The corresponding compound types were seen to be distributed more toward the sediment than toward the tube deposit. This same observation was noted in the discussion of solids formed during thermal stressing of fuel 2987 (Table VIII). Although the compositions with respect to nitrogen-containing compounds were similar in the sediments from the two fuels, fewer highly aromatic types were detected in the spectra of the sediment from fuel 2955. For example, only one homologue

for acridines and phenanthridines (mass 193) was identified in the 2955 spectra, but three were found in the spectra of the 2987 sediment (masses 179, 193, and 221), as noted in Table VIII. A few nitrogen-containing species were detected in the tube deposit from fuel 2955 as compared to virtually none in the spectra of the 2987 deposit (Table VIII). In this respect, several quinolines (or isoquinolines) were identified in the tube deposit from fuel 2955, but the presence of this compound type in the 2987 deposit was doubtful.

#### SUMMARY AND CONCLUSIONS

Storage and thermal stabilities of a JP-8 fuel produced from GPGP liquid by-products were compared with those of a conventional petroleum-derived JP-8 fuel. Initial characterization and simulated distillation of the two fuels showed that the coal-derived fuel contained more lower-boiling components, a longer filtration time, and a higher particulate content than the petroleum-derived fuel. Also, the coal-derived fuel possessed a slight color. Nevertheless, for the most part both fuels met JP-8 specifications.

Both fuels exhibited good oxidation stability through 40 hours of aging according to ASTM D 2274, with the coal-derived fuel showing less sediment and color formation but somewhat higher peroxide content than the petroleum-derived fuel. Storage stability (aging at 80° C under 100 psig oxygen) gave approximately the same results for both fuels through three weeks of aging. However, between the third and fourth week, the coal-derived fuel deteriorated rapidly and exceeded the petroleum fuel in sediment and color formation as well as peroxide content.

Fractionation of the 80° C aged sediment from the coal-derived fuel by HPLC indicated that the sediment was composed primarily of carboxylic acids and difunctional acids.

Both fuels easily met thermal-stability specifications with the coal-derived fuel showing a higher breakpoint temperature than the petroleum-derived fuel.

Mass spectra of the filterable sediments and JFTOT-tube deposits formed during thermal stressing of the coal-derived and petroleum-derived fuels were remarkably similar, indicating that the same compound types were responsible for solids formation in both fuels.

When spectra of the filterable sediment from either fuel were compared with those of the tube deposit from the same fuel, a number of similarities were found as well as some significant differences. Both sets of spectra showed molecular- and fragment-ion peaks for aromatic and nonaromatic hydrocarbons and for compounds containing one to three oxygens. Strong peaks were observed in the spectra of the filterable sediment corresponding to aromatic compounds containing one nitrogen. These peaks were much weaker or absent in the spectra from the tube deposit. No spectra of the sediment or tube deposit from either fuel showed more than traces of sulfur-containing compounds.

An intense, nonaromatic fragment ion containing three oxygens was identified in the spectra the tube deposits from both fuels. This ion was also found in the spectra of the filterable sediments from both fuels although its intensity was much weaker. The ion could not be correlated with a



molecular ion from any particular compound type, but it may have originated from an alcohol, ether, or some other type that does not produce a significant molecular ion.

Although structural information obtained through mass-spectral analysis of solids formed during thermal-stressing experiments has not specifically identified precursors responsible for solids formation in either fuel, the results demonstrate the value of the method for identifying compound types associated with fuel degradation under conditions of high temperature, such as those encountered in turbine engines.

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TABLE I  
INITIAL CHARACTERIZATION OF JP-8 FUELS DERIVED FROM  
PETROLEUM (2955) AND COAL (2987)

Property	Method	Fuel		Specification maximum
		2955	2987	
Color, Saybolt	D 156	+29	+14	---
Viscosity, -20 °C, cSt	D 445	4.8	4.4	8.0
Particulate, mg/mL	D 2276	0.26	1.2	1.0
Filtration time, min.	MIL-T-83133B, Appendix A	6.5	28	15
Peroxide, ppm	D 3703	0	0.5	---

TABLE II  
STORAGE-STABILITY RESULTS FOR PETROLEUM-DERIVED FUEL (2955)  
AND COAL-DERIVED FUEL (2987)

Aging Time	1 week		2 weeks		3 weeks		4 weeks	
	2955	2987	2955	2987	2955	2987	2955	2987
Fuel								
Property								
Filterable sedi- ment, mg/100 mL	0.8	0.3	1.3	0.5	1.5	1.0	2.7	9.1
Adherent sedi- ment, mg/100 mL	0.5	0.2	0.5	0.1	0.6	0.7	1.1	398
Total sediment, mg/100 mL	1.3	0.5	1.8	0.6	2.1	1.7	3.8	407
Peroxide, ppm (D 3703)	3.5	9.5	6.6	39.0	8.9	757	12.8	334
Color (D 1500)	L1.0	L0.5	L1.0	L0.5	L1.0	L0.5	L1.0	2.5

TABLE III  
SEPARATION OF SEDIMENT FROM COAL-DERIVED FUEL (2987) BY HPLC.  
YIELDS AND TYPICAL COMPOSITIONS.

Fraction	Yield, wt%	Typical composition
1	0.77	very weak acids, polynuclear aromatic hydrocarbons
2	1.21	2-3 ring pyrrolic benzologs
3	1.21	4-5 ring pyrrolic benzologs and hindered hydroxyaromatics
4	7.84	hydroxyaromatics
5	13.03	carboxylic acids
6	54.68	difunctional acids
Recovery	78.74	

TABLE IV  
THERMAL STABILITY RESULTS (ASTM D 3241) FOR  
PETROLEUM-DERIVED FUEL (2955) AND COAL-DERIVED FUEL (2987)

Property	Fuel		Specification maximum
	2955	2987	
Tube deposit rating at tube temp. of 260° C	1	1	3
Pressure drop, mm HG	0	0	25
Breakpoint, °C	275	295	---

TABLE V

MASS-SPECTROMETRIC ANALYSIS OF FILTERABLE SEDIMENT AND TUBE DEPOSIT  
FROM THERMALLY STRESSED FUEL 2987. IDENTIFICATION OF HYDROCARBONS.

Suggested origin <sup>1</sup>	Elemental composition: $C_nH_{2n+z}$	Homologous ions detected	
		Filter	Tube
	$z = +2$	---	---
	+1	71-155	71-183
Olefins, cycloalkanes (70)	0	70-140 <sup>2</sup>	70-140, 168 <sup>2</sup>
	-1	69-167	69-153
Dienes, cycloalkenes (68), bicycloalkanes	-2	68-194	68-194
	-3	81-207	81-179
Cyclic dienes (66), tricycloalkanes	-4	80-178	80-192
	-5	79-191	79-205
Alkylbenzenes (78)	-6	92, 106, 134, 148, 176, 190	78-162
	-7	77-189	77-203
Indans (118), tetralins	-8	76-188 <sup>3</sup>	76-188 <sup>3</sup>
	-9	75-173	75-187
Indenes (116), dihydronaphthalenes	-10	74-200 <sup>3</sup>	74-186 <sup>3</sup>
	-11	73-157	87-185, 213
Naphthalenes (128)	-12	114-142, 170-212 <sup>3</sup>	114-184 <sup>3</sup>
	-13	113-211	113-197
Acenaphthenes (154), biphenyls	-14	126, 154 <sup>3</sup>	126, 154-196 <sup>3</sup>
	-15	125-195	139-195
Acenaphthylenes (152), phenalenes, fluorenes	-16	152-194	152-208
	-17	151-193	151-207
Anthracenes (178), phenanthrenes	-18	150-206 <sup>3</sup>	164-220 <sup>3</sup>
	-19	163, 191, 205	163, 205
Methylenephenanthrenes (190), phenylnaphthalenes	-20	176, 190 <sup>3</sup>	176, 204, 218 <sup>3</sup>
	-21	189, 203	133, 189-217
Fluoranthenes, pyrenes (202)	-22	202	202, 216, 244
	-23	215	145, 215, 229

<sup>1</sup>Molecular mass of first member of homologous series in parentheses.

<sup>2</sup>Series may contain rearrangement ions.

<sup>3</sup>First members of series may represent rearrangement ions.

TABLE VI

MASS-SPECTROMETRIC ANALYSIS OF FILTERABLE SEDIMENT AND TUBE DEPOSIT  
FROM THERMALLY STRESSED FUEL 2987. IDENTIFICATION OF COMPOUNDS  
CONTAINING ONE OXYGEN.

Suggested Origin <sup>1</sup>	Elemental Composition: $C_n H_{2n+z} O$	Homologous Ions Detected Filter Tube
	$z = +2$	---
	+1	73
	---	---
Tetrahydrofurans (72)	0	72
	-1	71-113, 239
		71-127
Dihydrofurans (70)	-2	70-112
	-3	69-139
		69-139
Furans (68)	-4	68-110, 138
	-5	81-151
		81-165
Phenols (94)	-6	94-150
	-7	93-163, 191
		107-135
Dihydrobenzofurans (120), hydroxyindans	-8	120-162
	-9	105-175
		106-162 <sup>2</sup>
		105-161
Benzofurans (118), indanones	-10	104-188 <sup>2</sup>
	-11	131-201
		104-188 <sup>2</sup>
		131-173
Naphthols (144)	-12	130-214 <sup>2</sup>
	-13	143-199
		144-200
		157-185
Acenaphthenols (170)	-14	156-226 <sup>2</sup>
	-15	155-211, 253
		184, 198
		155-197
Dibenzofurans (168)	-16	168-210
	-17	181-209
		182, 196
		181-209
Fluorenones (180), phenalenones	-18	180-222
	-19	207
		---
	...	...
	...	...
	-22	218, 246
		---

<sup>1</sup>Molecular mass of first member of homologous series in parentheses.

<sup>2</sup>First member of series may represent rearrangement ion.

TABLE VII

MASS-SPECTROMETRIC ANALYSIS OF FILTERABLE SEDIMENT AND TUBE DEPOSIT  
FROM THERMALLY STRESSED FUEL 2987. IDENTIFICATION OF COMPOUNDS  
CONTAINING THREE OXYGENS.

Suggested Origin <sup>2</sup>	Elemental Composition: $C_nH_{2n+2}O_3$	Homologous Ions Detected	
		Filter	Tube
	$z = +2$	78,162	---
	+1	119-147	---
	0	104,146-174	---
	-1	131,145	---
	-2	116-172	242
	-3	129,157	129 <sup>3</sup> ,143, 185,241
	-4	100,128,170	100,128,142
	-5	141-183	127
	-6	154,182	---
	-7	167,181	---
	-8	166,208,222	152
	-9	221,235	151
	-10	150-178,220	---
	-11	149-191	149

<sup>1</sup>Peaks overlap with those containing one nitrogen.

<sup>2</sup>Multifunctional compounds.

<sup>3</sup>Very strong peak at  $m/z$  129.

TABLE VIII

MASS-SPECTROMETRIC ANALYSIS OF FILTERABLE SEDIMENT AND TUBE DEPOSIT  
FROM THERMALLY STRESSED FUEL 2987. IDENTIFICATION OF COMPOUNDS  
CONTAINING ONE NITROGEN.

Suggested Origin <sup>2</sup>	Elemental Composition: $C_nH_{2n+z}N$	Homologous Ions Detected	
		Filter	Tube
Aliphatic amines	$z = +3$	---	---
	$+2$	72-100	268,296 <sup>4</sup>
Pyrrolidines (71), piperidines	$+1$	85	---
	0	70-112	294 <sup>4</sup>
Pyrrolines (69)	-1	69-125,153	---
	-2	68-152	---
Pyrroles (67)	-3	81,95,123	---
	-4	80-150	---
Pyridines (79), anilines	-5	79-149	---
	-6	78-162	---
Indolines (119)	-7	91-175 <sup>3</sup>	---
	-8	76-174	---
Indoles (117)	-9	75,103-173 <sup>3</sup>	---
	-10	88-158,228	242 <sup>4</sup>
Quinolines (129), isoquinolines	-11	129-171	185,241 <sup>4</sup>
	-12	114-184	---
Phenylpyridines (155)	-13	127-183 <sup>3</sup>	---
	-14	140-196	---
Carbazoles (167)	-15	153-181 <sup>3</sup>	---
	-16	152,194,208	---
Acridines (179), phenan- thridines	-17	179,193,221	---
	-18	178,220	---
	-19	163-191	---
	-20	162-204,232	---
Aminofluoranthenes (217), aminopyrenes	-21	217	---
	-22	188,216-244	---

<sup>1</sup>Peaks overlap with those containing three oxygens.

<sup>2</sup>Molecular mass of first member of homologous series in parentheses.

<sup>3</sup>First members of series may represent rearrangement ions.

<sup>4</sup>Ions probably originate from different molecular structure.



TABLE V

MASS-SPECTROMETRIC ANALYSIS OF FILTERABLE SEDIMENT AND TUBE DEPOSIT  
FROM THERMALLY STRESSED FUEL 2987. IDENTIFICATION OF HYDROCARBONS.

Suggested origin <sup>1</sup>	Elemental composition: $C_nH_z$	Homologous ions detected	
		Filter	Tube
	$z = +2$	---	---
	+1	71-155	71-183
Olefins, cycloalkanes (70)	0	70-140 <sup>2</sup>	70-140, 168 <sup>2</sup>
	-1	69-167	69-153
Dienes, cycloalkenes (68), bicycloalkanes	-2	68-194	68-194
	-3	81-207	81-179
Cyclic dienes (66), tricycloalkanes	-4	80-178	80-192
	-5	79-191	79-205
Alkylbenzenes (78)	-6	92, 106, 134, 148, 176, 190	78-162
	-7	77-189	77-203
Indans (118), tetralins	-8	76-188 <sup>3</sup>	76-188 <sup>3</sup>
	-9	75-173	75-187
Indenes (116), dihydronaphthalenes	-10	74-200 <sup>3</sup>	74-186 <sup>3</sup>
	-11	73-157	87-185, 213
Naphthalenes (128)	-12	114-142, 170-212 <sup>3</sup>	114-184 <sup>3</sup>
	-13	113-211	113-197
Acenaphthenes (154), biphenyls	-14	126, 154 <sup>3</sup>	126, 154-196 <sup>3</sup>
	-15	125-195	139-195
Acenaphthylenes (152), phenalenes, fluorenes	-16	152-194	152-208
	-17	151-193	151-207
Anthracenes (178), phenanthrenes	-18	150-206 <sup>3</sup>	164-220 <sup>3</sup>
	-19	163, 191, 205	163, 205
Methylenephenanthrenes (190), phenylnaphthalenes	-20	176, 190 <sup>3</sup>	176, 204, 218 <sup>3</sup>
	-21	189, 203	133, 189-217
Fluoranthenes, pyrenes (202)	-22	202	202, 216, 244
	-23	215	145, 215, 229

<sup>1</sup>Molecular mass of first member of homologous series in parentheses.

<sup>2</sup>Series may contain rearrangement ions.

<sup>3</sup>First members of series may represent rearrangement ions.